PATENT SPECIFICATION

1,067,915

NO DRAWINGS

1,067,915

Date of Application and filing Complete Specification: Oct. 26, 1964.
No. 43599/64.
Application made in Germany (No. F41104 VIa/40b) on Oct. 26, 1963.
Complete Specification Published: May 10, 1967.

Index at acceptance:—C7 A(B23Y, B230, B235, B238, B24X, B242, B245, B247, B249, B279, B289, B29Y, B307, B309, B31Y, B310, B316, B319, B32Y, B331, B333, B335, B337, B339, B349, B35Y, B35X, B37Y, B383, B385, B387, B389, B39Y, B390, B394, B395, B396, B397, B419, B439, B459, B46Y, B470, B473, B475, B477, B479, B48X, B481, B483, B485, B487, B489, B519, B539, B549, B55Y, B555, B556, B557, B558, B610, B613, B614, B616, B617, B619, B62X, B621, B622, B624, B627, B630, B633, B635, B636, B66X, B661, B663, B665, B667, B669, B670)

Int. Cl.:—C 22 c 23/00

COMPLETE SPECIFICATION

Process for improving the Strength Properties and Oxidation Resistance of Zirconium-Containing Magnesium Alloys and Alloys produced by the process

We, FUCHS GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, of Meinerzhagen, Westphalia, Germany, a body corporate organised under the laws of Germany, personally responsible partner of the firm OTTO FUCHS do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to zirconium-containing magnesium alloys, and a method of improving the mechanical strength and oxidation resistance of zirconium-containing magnesium alloys.

In order to obtain high mechanical strengths in the earliest known aluminium, and possibly also zinc-containing magnesium alloys, the melts of these alloys must be submitted to grain refining processes, for instance to overheating or to a treatment with chlorine-containing hydrocarbons, such as hexachloroethane or other carbon compounds. However, these grain refining processes cannot be successfully applied to magnesium alloys containing no aluminium, such as alloys with zinc.

About 25 years ago Sauerwald, Eisenreich and Holub discovered that an addition of 0.05 to 2% by weight zirconium to unalloyed magnesium has a pronounced fining effect on the grain of the casting and at the same time improves its mechanical properties. The same workers further found that the grain refining effect of an addition of zirconium also applies to magnesium alloys containing alloying elements such as beryllium, lead, cadmium, calcium, cerium, copper, silver, thallium, thorium, bismuth and zinc which form no high melting intermetallic compounds with zirconium that are insoluble in the molten magnesium and therefore segregate. On the other hand, the elements aluminium, antimony, cobalt, manganese, nickel, silicon and tin form such high melting intermetallic compounds with zirconium that they are therefore unsuitable in principle as alloying elements for zirconium-containing magnesium alloys. However, it appears that in the case of a few of these elements it is nevertheless possible to alloy them with magnesium in the presence of small quantities of zirconium.

British metallurgists found that for instance small quantities of zirconium and manganese in specific proportions can be alloyed with magnesium. In this context they proposed magnesium alloys containing by weight 0.1 to 0.5% zirconium and 0.15 to 0.5% manganese with possible further alloying additions such as up to 1.25% of zinc and/or up to 3% of rare earth metals. They illustratively described a magnesium alloy containing 0.76% cerium, 0.26% manganese and 0.31% zirconium.

Later the inclusion of yttrium as a grain-refining addition to unalloyed magnesium and manganese-containing magnesium alloys was proposed by Sauerwald and Eisenreich who described magnesium alloys containing by weight 0.1 to 10% yttrium and possibly up to 2.5% manganese.

However, more recent investigations by the inventors and others have disclosed that the grain-refining and hence strength improving effect of an addition of yttrium is not very

considerable, and yttrium-containing magnesium alloys have not therefore assumed any importance in the technological field.

Quite unexpectedly, it has now been discovered that an addition of yttrium brings about a further refinement of the grain of a zirconium-containing magnesium alloy. A binary magnesium alloy containing 0.7% zirconium as cast has an average grain size of 0.15 mm., whereas a ternary magnesium alloy containing 0.7% zirconium as well as 0.9% yttrium has been found to have a mean grain size of only 0.06 mm. The mechanical properties of the yttrium-containing alloy at room temperature are correspondingly improved.

It is a remarkable fact, as was further found, that the high temperature properties of the alloys are also improved by the presence of yttrium.

It was finally found that yttrium has a protective effect against oxidation both in the molten liquid and solid state of the magnesium.

One aspect of the present invention therefore provides a method of improving the mechanical properties at room temperature and at elevated temperatures, and the oxidation resistance of a magnesium alloy containing 0.1 to 1% by weight of zirconium, wherein 0.1 to 10% by weight of yttrium is added as an alloying addition to said alloy.

Another aspect of the present invention provides magnesium alloys containing by weight 0.1 to 1%, preferably 0.6 to 0.9% zirconium, 0.1 to 10%, preferably 0.3 to 4%, yttrium, remainder magnesium with or without conventional impurities.

The present zirconium and yttrium-containing magnesium alloys may also contain additions totalling up to 10%, preferably up to 6% by weight of one or more alloying elements such as zinc, which do not form high melting intermetallic compounds. The protective effect of yttrium in relation to oxidation is of particular importance in the case of zirconium-containing magnesium alloys including at least one of the said alloying elements such as zinc.

The highest amounts of these additional alloying elements which may not be exceeded on technical grounds, differ for the various elements. The amount by weight of any one of these additional alloying elements which may be added in the absence of the others is set forth below, the upper value being exclusive. When two or more of these elements are present, experiments may have to be carried out to determine the maximum allowable amount of any one element in the presence of any other(s) that will not materially impair the high temperature properties of the ternary magnesium-zirconium-yttrium alloy.

beryllium 0 to 0.01%, preferably 0.001 to 0.005%

lead	0 to 10%
cadmium	0 to 10%
calcium	0 to 3%
cerium*	0 to 3%
copper	0 to 1%
silver	0 to 8%
thallium	0 to 10%
thorium	0 to 5%
bismuth	0 to 10%
zinc	0 to 7%

*including cerium and other rare earth elements.

The improvement of the mechanical properties at room temperature and at elevated temperatures, and of the resistance to oxidation due to an yttrium addition of preferably 0.3 to 4% also arises in magnesium alloys containing small quantities of zirconium and manganese, i.e. in alloy containing 0.1 to 0.5% zirconium and 0.15 to 0.5% manganese. These magnesium - zirconium - maganese-yttrium alloys, in the same way as the corresponding alloys lacking yttrium, may incidentally also contain up to 1.25% zinc and/or up to 3% of rare earth metals.

The high temperature properties of the ternary magnesium-zirconium-yttrium alloys are increasingly reduced by rising contents of alloying elements such as zinc and cadmium. If therefore alloys of improved high temperature properties are desired, alloying additions such as zinc and cadmium must remain within suitable limits to prevent them from impairing the improvement of the high temperature properties of ternary alloys by the addition of yttrium.

The present invention is illustrated by the following examples.

EXAMPLE 1.

The improvement in mechanical strength of a zirconium-containing magnesium alloy, as cast, at room temperature (20° C.) and at elevated temperatures due to an addition of yttrium is exemplified in the following

TABLE

	Binary magnesium alloy with 0.7% by weight Zr	Ternary magnesium alloy with 0.7% Zr and 0.9% Y by weight
Mean grain diameter	0.15 mm	0.06 mm.
Tensile strength (δ_B) at 20°C.	17.2 kg./mm.^{2}	18.2 kp./mm.^{2}
Yield point ($\delta_{0\cdot2}$) at 20°C.	5.2 kp./mm.^{2}	7.5 kp./mm.^{2}
Elongation (δ_5) at 20°C.	13.2%	20.0%
Contraction at 20°C.	14.7%	27.0%
Tensile strength (δ_B) at 450°C.	0.6 kp./mm.^{2}	1.2 kp./mm.^{2}
Yield strength ($\delta_{0\cdot2}$) at 450°C.	0.3 kp./mm.^{2}	1.0 kp./mm.^{2}
Tensile strength (δ_B) at 500°C.	0.42 kp./mm.^{2}	0.74 kp./mm.^{2}

At 500°C. the yield point could not be measured.

EXAMPLE 2.

Whereas binary magnesium-zirconium alloys, such as one containing 0.7% Zr by weight, exhibit the same tendency to scorch in the liquid molten state as all magnesium alloys lacking beryllium, a ternary magnesium alloy containing by weight 0.7% Zr and 0.9% Y hardly shows any such tendency. Tests have proved that this alloy can therefore be cast without being dusted with sulphur as is the practice. The anti-scorching effect of an addition of yttrium even exceeds the known effect of an addition of beryllium of 0.002%.

The anti-scorching effect of yttrium was also examined in the solid state. Sample castings of a binary magnesium alloy with 0.7% by weight zirconium and of a ternary alloy with 0.7% zirconium and 0.9% yttrium by weight were heated for six hours at 575° C. Whereas the samples of the binary alloy exhibited considerable traces of scorching and were completely covered with a white oxide skin after having been heated, the samples of the ternary alloy were unchanged and substantially free from oxidation.

WHAT WE CLAIM IS:—

1. A method of improving the mechanical properties at room temperature and at elevated temperatures, and the scorch resistance of a magnesium alloy containing 0.1 to 1% by weight of zirconium, wherein 0.1 to 10% by weight of yttrium is added as an alloying addition to said alloy.

2. A magnesium alloy comprising by weight 0.1 to 1% of zirconium, 0.1 to 10% yttrium, remainder magnesium with or without conventional impurities.

3. A magnesium alloy as claimed in Claim 2, wherein the zirconium content is 0.6 to 0.9% by weight and the yttrium content is 0.3 to 4% by weight.

4. A magnesium alloy as claimed in Claim 2 or 3, wherein the alloy contains a total of up to 10% by weight of at least one additional alloying element which is selected from beryllium, lead, cadmium, calcium, cerium, copper, silver, thallium, thorium, bismuth and zinc, and which forms no high melting intermetallic compounds with zirconium that are insoluble in the molten magnesium and segregate, the maximum amount of any one of said additional alloying elements in the absence of any of the others being as hereinbefore set forth.

5. A magnesium alloy as claimed in Claim 4, wherein the overall quantity of the specified additional alloying element(s) does not exceed 6%.

6. A magnesium alloy as claimed in Claim 4 or 5, wherein the quantity of the specified additional alloying element(s) is limited to a quantity that does not materially impair the high temperature properties of the ternary magnesium-zirconium-yttrium alloy.

7. A magnesium alloy as claimed in Claim 2, comprising by weight 0.1 to 0.5% zirconium, 0.3 to 4% yttrium, and 0.15 to 0.5% manganese.

8. A magnesium alloy as claimed in Claim 7, wherein the alloy contains up to 1.25% by weight zinc.

9. A magnesium alloy as claimed in Claim 7 or 8, wherein the alloy contains up to 3% of rare earth metals.

10. A magnesium-zirconium-yttrium alloy

in accordance with Claim 2 substantially as hereinbefore described in either of the foregoing Examples.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.
—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.